PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) **International Patent Classification:** **H01L 21/44, C23C 16/00**

A1

(11) **International Publication Number:** **WO 00/54320**

(43) **International Publication Date:** 14 September 2000 (14.09.2000)

(21) **International Application Number:** PCT/US00/02577

(22) **International Filing Date:** 01 February 2000 (01.02.2000)

(30) **Priority Data:**
09/267,953 11 March 1999 (11.03.1999) US

(60) **Parent Application or Grant**
GENUS, INC. [/]; (). SNEH, Ofer [/]; (). BOYS, Donald, R. ; ().

Published

(54) **Title: RADICAL-ASSISTED SEQUENTIAL CVD**

(54) **Titre: DCPV SEQUENTIEL ASSISTE PAR RADICAUX LIBRES**

(57) Abstract

A new method for CVD deposition on a substrate is taught wherein radical species are used in alternate steps to depositions from a molecular precursor to treat the material deposited from the molecular precursor and to prepare the substrate surface with a reactive chemical in preparation for the next molecular precursor step. By repetitive cycles a composite integrated film is produced. In a preferred embodiment the depositions from the molecular precursor are metals, and the radicals in the alternate steps are used to remove ligands left from the metal precursor reactions, and to oxidize or nitridize the metal surface in subsequent layers. A variety of alternative chemistries are taught for different films, and hardware combinations to practice the invention are taught as well.

(57) Abrégé

L'invention concerne un nouveau procédé de dépôt DCPV sur un substrat, dans lequel des espèces radicalaires sont utilisées dans des étapes en alternance avec des étapes de dépôts à partir d'un précurseur moléculaire pour le traitement de matériau déposé à partir dudit précurseur et pour la préparation de la surface de substrat à l'aide d'un produit chimique réactif en préparation pour l'étape suivante du précurseur moléculaire. Un film composite intégré est produit par des cycles répétés. Dans un mode de réalisation préféré, les dépôts à partir des précurseurs moléculaires sont des métaux, et les radicaux dans les étapes de remplacement sont utilisés pour supprimer les ligands à gauche des réactions du précurseur métallique, et pour oxyder ou nitrurer la surface du métal dans les couches suivantes. Plusieurs techniques chimiques sont présentées pour différents films, ainsi que des combinaisons de matériel pour la mise en oeuvre du procédé de l'invention.

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : H01L 21/44, C23C 16/00 — A1

(11) International Publication Number: WO 00/54320

(43) International Publication Date: 14 September 2000 (14.09.00)

(21) International Application Number: PCT/US00/02577

(22) International Filing Date: 1 February 2000 (01.02.00)

(30) Priority Data:
09/267,953 11 March 1999 (11.03.99) US

(71) Applicant: GENUS, INC. [US/US]; 1139 Karlstadt Drive, Sunnyvale, CA 94089 (US).

(72) Inventor: SNEH, Ofer; 11 Yellow Jacket Court, Branchburg, NJ 08876 (US).

(74) Agent: BOYS, Donald, R.; P.O. Box 187, Aromas, CA 95004 (US).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: RADICAL-ASSISTED SEQUENTIAL CVD

(57) Abstract

A new method for CVD deposition on a substrate is taught wherein radical species are used in alternate steps to depositions from a molecular precursor to treat the material deposited from the molecular precursor and to prepare the substrate surface with a reactive chemical in preparation for the next molecular precursor step. By repetitive cycles a composite integrated film is produced. In a preferred embodiment the depositions from the molecular precursor are metals, and the radicals in the alternate steps are used to remove ligands left from the metal precursor reactions, and to oxidize or nitridize the metal surface in subsequent layers. A variety of alternative chemistries are taught for different films, and hardware combinations to practice the invention are taught as well.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Description

Radical-Assisted Sequential CVD

Field of the Invention

The present invention is in the area of chemical vapor deposition, and pertains more particularly to new methods and apparatus for depositing films by atomic layer deposition.

Background of the Invention

In the manufacture of integrated circuits, deposition of thin films of many pure and compound materials is necessary, and many techniques have been developed to accomplish such depositions. In recent years the dominant technique for deposition of thin films in the art has been chemical vapor deposition (CVD), which has proven to have superior ability to provide uniform even coatings, and to coat relatively conformally into vias and over other high-aspect and uneven features in wafer topology. As device density has continued to increase and geometry has continued to become more complicated, even the superior conformal coating of CVD techniques has been challenged, and new and better techniques are needed.

The approach of a variant of CVD, Atomic Layer Deposition has been considered for improvement in uniformity and conformality, especially for low temperature deposition. However the practical implementation of this technology requires a solution to higher purity and higher throughput. This patent addresses these requirements.

Atomic Layer Deposition

In the field of CVD a process known as Atomic Layer Deposition (ALD) has emerged as a promising candidate to extend the abilities of CVD techniques, and is under rapid development by semiconductor equipment manufacturers to further improve characteristics of chemical vapor deposition. ALD is a process originally termed Atomic Layer Epitaxy, for which a competent reference is: Atomic Layer Epitaxy, edited by T. Suntola and M. Simpson, published by Blackie, Glasgo and London in 1990. This publication is incorporated herein by reference.

Generally ALD is a process wherein conventional CVD processes are divided into single-monolayer deposition steps, wherein each separate deposition step theoretically goes to saturation at a single molecular or atomic monolayer thickness, and self-terminates.

The deposition is the outcome of chemical reactions between reactive molecular precursors and the substrate. In similarity to CVD, elements composing the film are delivered as molecular precursors. The net reaction must deposit the *pure* desired film and eliminate the "extra" atoms that compose the molecular precursors (ligands). In the case of CVD the molecular precursors are fed simultaneously into the CVD reactor. A substrate is kept at temperature that is optimized to promote chemical reaction between the molecular precursors concurrent with efficient desorption of byproducts. Accordingly, the reaction proceeds to deposit the desired pure film.

For ALD applications, the molecular precursors are introduced into the ALD reactor separately. This is practically done by flowing one precursor at a time, i.e. a metal precursor – ML_x (M = Al, W, Ta, Si etc.) that contains a metal element – M which is bonded to atomic or molecular ligands – L to make a volatile molecule. The metal precursor reaction is typically followed by inert gas purging to eliminate this precursor from the chamber prior to the separate introduction of the other precursor. An ALD reaction will take place *only* if the surface is *prepared* to react directly with the molecular precursor. Accordingly the surface is typically prepared to include hydrogen-containing ligands - AH that are reactive with the metal precursor. Surface

– molecule reactions can proceed to react with all the ligands on the surface and deposit a monolayer of the metal with its passivating ligand: substrate -AH + $ML_x \rightarrow$ substrate-AML_y + HL, where HL is the exchange reaction by-product. During the reaction the initial surface ligands – AH are consumed and the surface becomes covered with L ligands, that cannot further react with the metal precursor – ML_x. Therefore, the reaction self-saturates when all the initial ligands are replaced with – ML_y species.

After completing the metal precursor reaction the excess precursor is typically removed from the reactor prior to the introduction of another precursor. The second type of precursor is used to restore the surface reactivity towards the metal precursor, i.e. eliminating the L ligands and redepositing AH ligands.

Most ALD processes have been applied to deposit compound films. In this case the second precursor is composed of a desired (usually nonmetallic) element – A (i.e. O, N, S), and hydrogen using, for example H_2O, NH_3, or H_2S. The reaction: -ML – $AH_z \rightarrow$ -M-AH + HL (for the sake of simplicity the chemical reactions are not balanced) converts the surface back to be AH-covered. The desired additional element – A is deposited and the ligands L are eliminated as volatile by-product. Again, the reaction consumes the reactive sites (this time the L terminated sites) and self-saturates when the reactive sites are entirely depleted.

The sequence of surface reactions that restores the surface to the initial point is called the ALD *deposition cycle*. Restoration to the initial surface is the ***keystone*** of ALD. It implies that films can be layered down in equal metered sequences that are all identical in chemical kinetics, deposition per cycle, composition and thickness. Self-saturating surface reactions make ALD insensitive to transport nonuniformity either from flow engineering or surface topography (i.e. deposition into high aspect ratio structures). Non uniform flux can only result in different completion time at different areas. However, if each of the reactions is allowed to complete on the entire area, the different completion kinetics bear no penalty.

As is often the case with process development, the initial promised advantages of a new technique do not, in the end, attain their full initial promise. Unfortunately, ALD has a serious fundamental problem. Unlike CVD reactions that are of a

continuous steady state nature, ALD reactions follow kinetics of molecular-surface interaction. Kinetics of molecular- surface reactions depends on the individual reaction rate between a molecular precursor and a surface reactive site and the number of available reactive sites. As the reaction proceeds to completion, the surface is converted from being reactive to non-reactive. As a result the reaction rate is slowing down during the deposition. In the simplest case the rate, dN/dt is proportional to the number of reactive sites, $dN/dt = -kN$, where N is the number of reactive sites and k is the (single site) reaction rate. Eliminating reactive sites (or growing of the *already-reacted* sites) follows an exponential time dependence $kN(t) = kN_0 exp(-kt)$. This fundamental property of molecule-surface kinetics was named after the great scientist Langmuir, and is quite well-known in the art.

The interpretation of Langmuirian kinetics limitations illustrates a serious drawback of ALD and a severe deviation from the *ideal* picture. Accordingly, the self-terminating reactions never really self-terminate (they would require an infinite time because the rate is exponentially decreasing). It means that under practical conditions the surface is never entirely reacted to completion after a *deposition cycle*. If the surface is not completely reacted there are leftover undesired elements in the film. For example, if the ML_x reaction cannot totally consume the surface –AH sites, the film will have H incorporation. Likewise, if the AH_y reaction is not carried to completion, undesired L incorporation is inevitable. Clearly, the quality of the film depends on the impurity levels. The *throughput-quality tradeoff* is of particular concern because it carries an exponential throughput penalty to attain a reduction of impurity levels.

In conventional atomic layer deposition one must accept low throughput to attain high-purity film, or accept lower-purity films for higher throughput. What is clearly needed is an apparatus and methods which not only overcome the Langmuirian limitations but simultaneously provide higher-purity films than have been available in the prior art methods. Such apparatus and methods are provided in embodiments of the present invention, taught in enabling detail below.

Summary of the Invention

In a preferred embodiment of the present invention a method for depositing a metal on a substrate surface in a deposition chamber is provided, comprising steps of (a) depositing a monolayer of metal on the substrate surface by flowing a molecular precursor gas or vapor bearing the metal over a surface of the substrate, the surface saturated by a first reactive species with which the precursor will react by depositing the metal and forming reaction product, leaving a metal surface covered with ligands from the metal precursor and therefore not further reactive with the precursor; (b) terminating flow of the precursor gas or vapor; (c) purging the precursor with inert gas; (d) flowing at least one radical species into the chamber and over the surface, the radical species highly reactive with the surface ligands of the metal precursor layer and eliminating the ligands as reaction product, and also saturating the surface, providing the first reactive species; and (e) repeating the steps in order until a metallic film of desired thickness results.

In many such embodiments the radical species is atomic hydrogen. Using atomic hydrogen a broad variety of pure metals may be deposited, such as tungsten, tantalum, aluminum, titanium, molybdenum, zinc, hafnium, niobium and copper.

In another aspect of the invention a method is provided for depositing a metal oxide on a substrate surface in a deposition chamber, comprising steps of (a) depositing a monolayer of metal on the substrate surface by flowing a metal molecular precursor gas or vapor bearing the metal over a surface of the substrate, the surface saturated by a first reactive species with which the precursor will react by depositing the metal and forming reaction product, leaving a metal surface covered with ligands from the metal precursor and therefore not further reactive with the precursor; (b) terminating flow of the precursor gas or vapor; (c) purging the precursor with inert gas; (d) flowing a first radical species into the chamber and over the surface, the radical species highly reactive with the reaction product and combining with the reaction product to create volatile species and saturate the surface with the first radical species; (e) flowing radical oxygen into the chamber to combine with the metal monolayer deposited in step (a), forming an oxide of the metal; (f)

flowing a third radical species into the chamber terminating the surface with the first reactive species in preparation for a next metal deposition step; and (g) repeating the steps in order until a composite film of desired thickness results.

In this method the first and third radical species may be both atomic hydrogen, and the metal surface in step (f) is terminated with hydroxyl species reactive with the metal precursor to deposit the metal. In another embodiment the oxygen and hydrogen atomic steps (e) and (f) are repeated to improve film quality. In still another embodiment steps (e) and (f) are combined into one step wherein the surface is reacted with hydrogen and oxygen atoms simultaneously.

In various embodiments for depositing oxides the oxides can be tantalum pentoxide, aluminum oxide, titanium oxide, niobium pentoxide, zirconium oxide, hafnium oxide, zinc oxide, molybdenum oxide, manganese oxide, tin oxide, indium oxide, tungsten oxide and silicon oxide, among others.

In some embodiments the first radical species is atomic hydrogen and steps (e) and (f) are united to one step using OH radicals, and the metal surface in step (f) is terminated with hydroxyl species reactive with the metal precursor to deposit the metal.

In still another aspect of the invention a method for depositing a metal nitride on a substrate surface in a deposition chamber is provided, comprising steps of (a) depositing a monolayer of metal on the substrate surface by flowing a metal precursor gas or vapor bearing the metal over a surface of the substrate, the surface saturated by a first reactive species with which the precursor will react by depositing the metal and forming reaction product, leaving a metal surface covered with ligands from the metal precursor and therefore not further reactive with the precursor; (b) terminating flow of the precursor gas or vapor; (c) purging the precursor with inert gas; (d) flowing a first radical species into the chamber and over the surface, the atomic species highly reactive with the surface ligands of the metal precursor layer and eliminating the ligands as reaction product and also saturating the surface; (e) flowing radical nitrogen into the chamber to combine with the metal monolayer deposited in step (a), forming a nitride of the metal; (f) flowing a third radical species into the chamber terminating the surface with the first reactive species in preparation for a next metal

deposition step; and (g) repeating the steps in order until a composite film of desired thickness results.

In this method the first and third atomic radical species may both be atomic hydrogen, and the metal surface in step (f) may be terminated with amine species reactive with the metal precursor to deposit the metal. Further, steps (e) and (f) may be combined into one step wherein the surface is reacted with hydrogen and nitrogen atoms simultaneously.

In variations of this embodiment a variety of different nitrides may be produces, including, but limited to tungsten nitride, tantalum nitride, aluminum nitride, titanium nitride, silicon nitride and gallium nitride.

In another variation the first radical species may be atomic hydrogen and steps (e) and (f) may be united into one step using one or both of NH and NH_2 radicals, and the metal surface in step (f) is terminated with amine species reactive with the metal precursor to deposit the metal.

In yet another aspect of the invention a process for building a metal, metal oxide, or metal nitride film on a substrate surface is provided, wherein deposition steps comprise flowing a metal precursor gas or vapor over the surface with the surface terminated with a first chemical species reactive with the metal precursor to deposit the metal, are alternated with steps comprising flowing radical species over the freshly deposited metal layers to remove the ligands from the deposition steps and to provide the first chemical species to terminate the substrate surface preparatory to the next deposition reaction.

In this process a metal nitride film is built up by a step sequence of metal deposition by reacting a metal precursor gas with a surface terminated by amine species, then alternating exposure of the surface with atomic radical hydrogen, nitrogen and hydrogen again, thereby volatilizing products remaining from the metal deposition chemistry, nitridizing the deposited metal monolayer, then terminating the metal surface with amine species again in preparation for a next metal deposition step. A metal oxide film is built up by a step sequence of metal deposition by reacting a metal precursor gas with a surface terminated by hydroxyl species, then alternating exposure of the surface with atomic radical hydrogen, oxygen and hydrogen again,

thereby volatilizing products remaining from the metal deposition chemistry, oxidizing the metal monolayer, then terminating the metal surface with hydroxyl species again in preparation for a next metal deposition step.

In yet another aspect of the invention a method for depositing a compound film on a substrate surface in a deposition chamber is provided, comprising steps of (a) depositing a monolayer of metal on the substrate surface by flowing a metal molecular precursor gas or vapor bearing the metal over a surface of the substrate, the surface saturated by a first reactive species with which the precursor will react by depositing the metal and forming reaction product, leaving a metal surface covered with ligands from the metal precursor and therefore not further reactive with the precursor; (b) terminating flow of the precursor gas or vapor; (c) purging the precursor with inert gas; (d) flowing a first radical species into the chamber and over the surface, the radical species highly reactive with the reaction product and combining with the reaction product to create volatile species and saturate the surface with the first radical species; (e) flowing nonmetal atomic species into the chamber to combine with the metal monolayer deposited in step (a), forming a compound film of the metal; (f) flowing a third radical species into the chamber terminating the surface with the first reactive species in preparation for a next metal deposition step; and (g) repeating the steps in order until a composite film of desired thickness results.

In this method the first and third radical species may be both atomic hydrogen, and the metal surface in step (f) is terminated with hydride species of the nonmetallic element that are reactive with the metal precursor to deposit the metal. In a variation the non-metallic and hydrogen atomic steps (e) and (f) are repeated to improve the film quality. In another variation steps (e) and (f) are combined into one step wherein the surface is reacted with hydrogen and non-metallic atoms simultaneously. A variety of films may be produced by practicing this variation of the invention as well, including but not limited to molybdenum disulfide and zinc sulfide.

In yet another aspect of the invention a radical-assisted sequential CVD (RAS-CVD) reactor is provided, comprising a chamber with controlled gas inlets for introducing gases in sequential steps and a heated substrate support for holding a substrate and exposing a surface of the substrate to incoming gases; and a plasma

generation apparatus for generating radical atomic species for use in the reactor. In this reactor an aggregate metal layer is formed by depositing a monolayer of metal on the substrate surface by flowing a precursor gas or vapor bearing the metal over a surface of the substrate, the surface terminated by a first reactive species with which the precursor will react by depositing the metal and forming reaction product, leaving a metal surface not further reactive with the precursor, terminating flow of the precursor gas or vapor, flowing at least one atomic radical species into the chamber and over the surface, the atomic species highly reactive with the reaction product and combining with the reaction product, and also terminating the surface, providing the first reactive species, and repeating the steps in order until a composite film of desired thickness results.

In various embodiments the atomic radical species is atomic hydrogen. The precursor gas bearing the metal may be tungsten hexafluoride and the metal deposited tungsten.

In some embodiments the plasma generation apparatus comprises an electrode within the reactor chamber and a high frequency power supply connected to the electrode. In other embodiments the plasma generation apparatus comprises a showerhead-type gas distribution apparatus, and a plasma is generated within the showerhead apparatus to produce the radical species. In still other embodiments the atomic radical species is produced in a remote plasma generator, and the species are delivered to the reactor.

In the various embodiments of the invention a new process is provided wherein films of many sorts, including pure metals, oxides of metals, nitrides of metals, and other films, may be produced quickly and efficiently, with very high purity and with superior conformity to substrate topography and coverage within vias and other difficult surface geometries.

Brief description of the Drawings

Fig. 1 is a generalized diagram of a reactor and associated apparatus for practicing a radical-assisted sequential CVD process according to an embodiment of the present invention.

Fig. 2 is a step diagram illustrating the essential steps of an atomic layer deposition process.

Fig. 3 is a step diagram illustrating steps in a radical-assisted CVD process according to an embodiment of the present invention.

Description of the Preferred Embodiments

The inventor has developed an enhanced variation of ALD which alters the conventional surface preparation steps of ALD and overcomes the problems of conventional ALD, producing high throughput without compromising quality. The inventor terms the new and unique process *Radical-Assisted Sequential CVD* (RAS-CVD).

Fig. 1 is a generalized diagram of a system 11 for practicing RAS-CVD according to an embodiment of the present invention. In this exemplary system a deposition chamber 13 has a heatable hearth for supporting and heating a substrate 19 to be coated, and a gas distribution apparatus, such as a showerhead 15, for delivering gaseous species to the substrate surface to be coated. Substrates are introduced and removed from chamber 13 via a valve 21 and substrate-handling apparatus not shown. Gases are supplied from a gas sourcing and pulsing apparatus 23, which includes metering and valving apparatus for sequentially providing gaseous materials. An optional treatment apparatus 25 is provided for producing gas radicals from gases supplied from apparatus 23.

The term *radicals* is well-known and understood in the art, but will be qualified again here to avoid confusion. By a *radical* is meant an unstable species. For example, oxygen is stable in diatomic form, and exists principally in nature in this

form. Diatomic oxygen may, however, be caused to split to monatomic form, or to combine with another atom to produce ozone, a molecule with three atoms. Both monatomic oxygen and ozone are *radical* forms of oxygen, and are more reactive than diatomic oxygen. In many cases in embodiments of the present invention the *radicals* produced and used are single atom forms of various gases, such as oxygen, hydrogen, and nitrogen, although the invention is not strictly limited to monatomic gases.

Fig. 2 is a step diagram of a conventional Atomic Layer Deposition process, and is presented here as contrast and context for the present invention. In conventional ALD, as shown in Fig. 2, in step 31 a first molecular precursor is pulsed in to a reactor chamber, and reacts with the surface to produce (theoretically) a monolayer of a desired material. Often in these processes the precursor is a metal-bearing gas, and the material deposited is the metal; Tantalum from $TaCl_5$, for example.

In step 33 in the conventional process an inert gas is pulsed into the reactor chamber to sweep excess first precursor from the chamber.

In step 35 in the conventional system a second precursor, typically non-metallic, is pulsed into the reactor. The primary purpose of this second precursor is to condition the substrate surface back toward reactivity with the first precursor. In many cases the second precursor also provides material from the molecular gas to combine with metal at the surface, forming compounds such as an oxide or a nitride with the freshly-deposited metal.

At step 37 the reactor chamber is purged again to remove excess of the second precursor, and then step 31 is repeated. The cycle is repeated as many times as is necessary to establish a desired film.

Fig. 3 is a step diagram illustrating steps in a radical-assisted CVD process according to an embodiment of the present invention. In the unique process illustrated by Fig. 3 the first steps, steps 41 and 43, are the same as in the conventional process. A first precursor is pulsed in step 41 to react with the substrate surface forming a monolayer of deposit, and the chamber is purges in step 43. The next step is unique. In step 45 single or multiple radical species are pulsed to the substrate surface to optionally provide second material to the surface and to condition the

surface toward reactivity with the first molecular precursor in a subsequent step. Then step 41 is repeated. There is no need for a second purge, and the cycle is repeated as often as necessary to accomplish the desired film.

Step 45 may be a single step involving a single radical species. For example, the first precursor may deposit a metal, such as in W from WF_6, and the radical species in step 45 may be atomic hydrogen. The atomic hydrogen very quickly and effectively neutralizes any remaining F to HF, and terminates the surface with atomic hydrogen, providing reactive surface for the next pulse of WF_6.

In many cases step 45 will be a compound step comprising substeps involving different radical species. A good example is a sequence of atomic hydrogen followed by atomic oxygen, followed by atomic hydrogen again. The first hydrogen step neutralizes Cl or other remaining ligand, the atomic oxygen provides an oxide of the freshly-deposited metal, and the second atomic hydrogen terminated the surface with (OH) in preparation for the next metal precursor step.

There are a broad variety of materials and combinations in step 45, and many are disclosed in more detail below, along with a more complete explanation of process chemistry.

In RAS-CVD, following the metal precursor reaction, highly reactive radical species are introduced to quickly react with products of the metal precursor reaction and to prepare the surface for the next metal precursor reaction. Radical species, as introduced above, are reactive atoms or molecular fragments that are chemically unstable and therefore are extremely reactive. In addition, radicals chemisorb to surfaces with virtually 100% efficiency. Radicals may be created in a number of ways, and plasma generation has been found to be an efficient and compatible means of preparation.

RAS-CVD processes use only a single molecular precursor, in many cases a metal precursor. Surface preparation as well as the deposition of nonmetallic elements are accomplished by atom-surface reactions. Following the metal precursor reaction, The –ML terminated surface is reacted with hydrogen atoms to convert the surface into –MH and eliminate HL by-product. Unlike molecule-surface reactions, atom-surface reactions do not depend on the number density of reactive sites. Most

atoms (except for noble gases) stick very efficiently to surfaces in an irreversible process because atomic desorption is usually unfavorable. The atoms are highly mobile on non-reactive sites and very reactive at reactive sites. Consequently, atom-surface reactions have linear exposure dependence, as well as high rates.

The -MH surface can be reacted with A atoms to yield a –M-A- surface. In this case some of the H ligands can be eliminated as AH_y. For example the -MH surface can be reacted with oxygen atoms to deposit oxide compound. Alternatively, -MH surface can be reacted again with ML_x for atomic layer controlled deposition of M metal films. For the deposition of nitride compound films, A is atomic nitrogen. The surface after the A atomic reaction is terminated with A- and AH. At this point an additional atomic reaction with hydrogen converts the surface to the desired AH ligands that are reactive towards the metal precursor. Alternatively, the MH surface can be reacted with a mixture of A and H atoms to convert the surface into –AH terminated surface with one less step. All the above described reactions are radical-surface reactions that are fast and efficient and depend linearly on exposure. In addition, the final hydrogen reaction results in a complete restoration to the initial surface without any incorporation of impurities.

Another throughput benefit of RAS-CVD is that a single purge step after the metal precursor step is needed, rather than the two purge steps needed in the conventional process. Purge steps are expected by most researchers to be the most significant throughput-limiting step in ALD processes. Another advantage is that RAS-CVD promises longer system uptime and reduced maintenance. This is because atomic species can be efficiently quenched on aluminum walls of the deposition module. Downstream deposition on the chamber and pumping lines is therefore virtually eliminated. RAS-CVD eliminates the use of H_2O and NH_3 that are commonly applied for oxides and nitrides deposition (respectively) in the prior art. These precursors are notorious to increase maintenance and downtime of vacuum systems.

According to the above a typical RAS-CVD cycle for a metal oxide film will comprise steps as follows:

1. Metal precursor reaction with –OH (hydroxyl) terminated surface to attach –O-ML_y and eliminate the hydrogen by HL desorption. The surface becomes covered with L ligands, i.e. in the case of $TaCl_5$ the surface becomes covered with Cl atoms.
2. Purge with inert gas to sweep away excess metal precursor.
3. Atomic hydrogen step – eliminates the ligands L by HL desorption and terminates the surface with hydrogen.
4. Atomic oxygen step - reacts with monolayer of metal to form oxide. Atomic hydrogen again to leave hydroxyl saturated surface for next metal precursor step.

At this point the quality of oxide films (i.e. insulation properties, dielectric strength, charge trapping) can be improved by running steps 4–5 for multiple times. For example. Al_2O_3 RAS-CVD can be realized from trimethylaluminum $Al(CH_3)_3$, hydrogen and oxygen exposures. $Al(CH_3)_3$ reacting with –OH terminated surface will deposit $–OAl(CH_3)_x$ concurrent with the desorption of methane (CH_4). The $–OAl(CH_3)_x$ (x=1,2) surface will be treated with H atoms to eliminate x number of methane molecules and terminate the surface with –OAlH. This surface after consecutive (or concurrent) reaction with O atoms and H atoms will be terminated –OAl-OH which is the restoration state. At this point, the RAS-CVD process can proceed by applying another $Al(CH_3)_3$ reaction. Alternatively, the –OAl-OH surface can be exposed to another cycles of O and H atoms. At temperature above 100 °C this process will exchange OH groups and Al-O-Al bridge sites and the resulted –OAl-OH surface will be more thermodynamically favorable than the beginning surface, because the process eliminates the more strained $(Al\text{-}O\text{-})_n$ ring structures as well as titrating away defects and broken bonds). Since the atomic reactions are rather fast, these quality improvements are not expected to be a major throughput concern. In fact, ultimate quality may be achieved by applying the O, H cycles for several times. Following, a given number of O, H atomic reactions the sequence will continue with the next $Al(CH_3)_3$ reaction.

6. Repeat steps from 1.

For metal nitrides atomic nitrogen is substituted for oxygen. For pure metal depositions the oxygen/nitrogen step may be eliminated in favor of a single atomic hydrogen step, such as for tungsten films. The hydrogen saturated surface after the first atomic hydrogen step is reactive with WF_6 to produce the pure metal.

The generic nature of RAS-CVD is advantageous for multiple layer combination films of different oxides, different nitrides, oxides with nitrides, different metals and metals with compound films.

In another unique process, useful for barrier layers, the WN process may be combined with the pure W process to produce alternating W and WN layers in a variety of schemes to suppress polycrystallization and to reduce the resistivity of the barrier layer. Other properties, such as electromigration may be controlled by an ability to provide a graded layer of WN with reduced nitrogen content at the copper interface for such applications.

In embodiments of the invention a broad variety of process chemistries may be practiced, providing a broad variety of final films. In the area of pure metals, for example, the following provides a partial, but not limiting list:

1. Tungsten from tungsten hexafluoride.
2. Tantalum from tantalum pentachloride.
3. Aluminum from either aluminum trichloride or trimethylaluminum.
4. Titanium from titanium tetrachloride or titanium tetraiodide.
5. Molybdenum from molybdenum hexafluoride.
6. Zinc from zinc dichloride.
7. Hafnium from hafnium tetrachloride.
8. Niobium from niobium pentachloride.
9. Copper from Cu_3Cl_3.

In the area of oxides the following is a partial but not limiting list:

1. Tantalum pentoxide from tantalum pentachloride.
2. Aluminum oxide from trimethylaluminum or aluminum trichloride.
3. Titanium oxide. from titanium tetrachloride or titanium tetraiodide.
4. Niobium pentoxide from niobium pentachloride.
5. Zirconium oxide from zirconium tetrachloride.
6. Hafnium oxide from hafnium tetrachloride.
7. Zinc oxide from zinc dichloride.
8. Molybdenum oxide from molybdenum hexafluoride or molybdenum pentachloride.
9. Manganese oxide from manganese dichloride.
10. Tin oxide from tin tetrachloride.
11. Indium oxide from indium trichloride or trimethylindium.
12. Tungsten oxide from tungsten hexafluoride.
13. Silicon dioxide from silicon tetrachloride.

In the area of nitrides, the following is a partial but not limiting list:

1. Tungsten nitride from tungsten hexafluoride.
2. Tantalum nitride from tantalum pentachloride.
3. Aluminum nitride from aluminum trichloride or trimethylaluminum.
4. Titanium nitride from titanium tetrachloride.
5. Silicon nitride from silicon tetrachloride or dichlorosilane.
6. Gallium nitride from trimethylgallium.

Hardware Requirements

Another advantage of RAS-CVD is that it is compatible in most cases with ALD process hardware. The significant difference is in production of atomic species and/or other radicals, and in the timing and sequence of gases to the process chamber. Production of the atomic species can be done in several ways, such as (1) in-situ plasma generation, (2) intra-showerhead plasma generation, and (3) external generation by a high-density remote plasma source or by other means such as UV

dissociation or dissociation of metastable molecules. referring again to Fig. 1, these methods and apparatus are collectively represented by apparatus 25.

Of the options, in-situ generation is the simplest design, but poses several problems, such as turn on - turn off times that could be a throughput limitation. Intra-showerhead generation has been shown to have an advantage of separating the atomic specie generation from the ALD space. The preferable method at the time of this specification is remote generation by a high-density source, as this is the most versatile method. The radicals are generated in a remote source and delivered to the ALD volume, distributed by a showerhead over the wafer in process.

It will be apparent to the skilled artisan that there are a variety of options that may be exercised within the scope of this invention as variations of the embodiments described above.. some have already been described. For example, radicals of the needed species, such as hydrogen, oxygen, nitrogen, may be generated in several ways and delivered in the process steps. Further, ALD chambers, gas distribution, valving. timing and the like may vary in many particulars. Still further, many metals, oxides nitrides and the like may be produced, and process steps may be altered and interleaved to create graded and alternating films.

In addition to these variations it will be apparent to the skilled artisan that one may. by incorporating processes described herein, alternate process steps in a manner that alloys of two, three or more metals may be deposited, compounds may be deposited with two, three or more constituents. and such things as graded films and nano-laminates may be produced as well. These variations are simply variants using particular embodiments of the invention in alternating cycles, typically in-situ. There are many other variations within the spirit and scope of the invention, so the invention is limited only by the claims that follow.

Claims

What is claimed is:

1. A method for depositing a metal on a substrate surface in a deposition chamber, comprising steps of:

(a) depositing a monolayer of metal on the substrate surface by flowing a molecular precursor gas or vapor bearing the metal over a surface of the substrate, the surface saturated by a first reactive species with which the precursor will react by depositing the metal and forming reaction product, leaving a metal surface covered with ligands from the metal precursor and therefore not further reactive with the precursor;

(b) terminating flow of the precursor gas or vapor;

(c) purging the precursor with inert gas;

(d) flowing at least one radical species into the chamber and over the surface, the radical species highly reactive with the surface ligands of the metal precursor layer and eliminating the ligands as reaction product, and also saturating the surface, providing the first reactive species; and

(e) repeating the steps in order until a metallic film of desired thickness results.

2. The method of claim 1 wherein the radical species is atomic hydrogen.

3. The method of claim 1 wherein the precursor gas bearing the metal is tungsten hexafluoride and the metal deposited is tungsten.

4. The method of claim 1 wherein the precursor gas bearing the metal is tantalum pentachloride and the metal deposited is tantalum.

5. The method of claim 1 wherein the precursor gas bearing the metal is one of trimethylaluminum or aluminum trichloride and the metal deposited is aluminum.

6. The method of claim 1 wherein the precursor gas bearing the metal is one of titanium tetrachloride or titanium tetraiodide and the metal deposited is titanium.

7. The method of claim 1 wherein the precursor gas bearing the metal is molybdenum hexafluoride and the metal deposited is molybdenum.

8. The method of claim 1 wherein the precursor gas bearing the metal is zinc dichloride and the metal deposited is zinc.

9. The method of claim 1 wherein the precursor gas bearing the metal is hafnium tetrachloride and the metal deposited is hafnium.

10. The method of claim 1 wherein the precursor gas bearing the metal is niobium pentachloride and the metal deposited is niobium.

11. The method of claim 1 wherein the precursor gas is copper chloride Cu_3Cl_3 and the metal deposited is copper.

12. A method for depositing a metal oxide on a substrate surface in a deposition chamber, comprising steps of:

(a) depositing a monolayer of metal on the substrate surface by flowing a metal molecular precursor gas or vapor bearing the metal over a surface of the substrate, the surface saturated by a first reactive species with which the precursor will react by depositing the metal and forming reaction product, leaving a metal surface covered with ligands from the metal precursor and therefore not further reactive with the precursor;

(b) terminating flow of the precursor gas or vapor;

(c) purging the precursor with inert gas;

(d) flowing a first radical species into the chamber and over the surface, the radical species highly reactive with the reaction product and combining with the

reaction product to create volatile species and saturate the surface with the first radical species;

(e) flowing radical oxygen into the chamber to combine with the metal monolayer deposited in step (a), forming an oxide of the metal;

(f) flowing a third radical species into the chamber terminating the surface with the first reactive species in preparation for a next metal deposition step; and

(g) repeating the steps in order until a composite film of desired thickness results.

13. The method of claim 12 wherein the first and third radical species are both atomic hydrogen, and the metal surface in step (f) is terminated with hydroxyl species reactive with the metal precursor to deposit the metal.

14. The method of claim 13 wherein the oxygen and hydrogen atomic steps (e) and (f) are repeated to improve film quality.

15. The method of claim 12 wherein steps (e) and (f) are combined into one step wherein the surface is reacted with hydrogen and oxygen atoms simultaneously.

16. The method of claim 12 wherein the metal precursor is tantalum pentachloride and the film is tantalum pentoxide.

17. The method of claim 12 wherein the metal precursor is trimethylaluminum or aluminum trichloride and the film is aluminum oxide.

18. The method of claim 12 wherein the metal precursor is titanium tetrachloride or titanium tetraiodide and the film is titanium oxide.

19. The method of claim 12 wherein the metal precursor is niobium pentachloride and the film is niobium pentoxide.

20. The method of claim 12 wherein the metal precursor is zirconium tetrachloride and the film is zirconium oxide.

21. The method of claim 12 wherein the metal precursor is hafnium tetrachloride and the film is hafnium oxide.

22. The method of claim 12 wherein the metal precursor is zinc dichloride and the film is zinc oxide.

23. The method of claim 12 wherein the metal precursor is molybdenum hexafluoride or molybdenum pentachloride and the film is molybdenum oxide.

24. The method of claim 12 wherein the metal precursor is manganese dichloride and the film is manganese oxide.

25. The method of claim 12 wherein the metal precursor is tin tetrachloride and the film is tin oxide.

26. The method of claim 12 wherein the metal precursor is indium trichloride or trimethylindium and the film is indium oxide.

27. The method of claim 12 wherein the metal precursor is tungsten hexafluoride and the film is tungsten oxide.

28. The method of claim 12 wherein the metal precursor is silicon tetrachloride and the film is silicon dioxide.

29. The method of claim 12 wherein the first radical species is atomic hydrogen and steps (e) and (f) are united to one step using OH radicals, and the metal surface in step (f) is terminated with hydroxyl species reactive with the metal precursor to deposit the metal.

30. A method for depositing a metal nitride on a substrate surface in a deposition chamber, comprising steps of:

(a) depositing a monolayer of metal on the substrate surface by flowing a metal precursor gas or vapor bearing the metal over a surface of the substrate, the surface saturated by a first reactive species with which the precursor will react by depositing the metal and forming reaction product, leaving a metal surface covered with ligands from the metal precursor and therefore not further reactive with the precursor;

(b) terminating flow of the precursor gas or vapor;

(c) purging the precursor with inert gas;

(d) flowing a first radical species into the chamber and over the surface, the atomic species highly reactive with the surface ligands of the metal precursor layer and eliminating the ligands as reaction product and also saturating the surface;

(e) flowing radical nitrogen into the chamber to combine with the metal monolayer deposited in step (a), forming a nitride of the metal;

(f) flowing a third radical species into the chamber terminating the surface with the first reactive species in preparation for a next metal deposition step; and

(g) repeating the steps in order until a composite film of desired thickness results.

31. The method of claim 30 wherein the first and third atomic radical species are both atomic hydrogen, and the metal surface in step (f) is terminated with amine species reactive with the metal precursor to deposit the metal.

32. The method of claim 31 wherein steps (e) and (f) are combined to one step wherein the surface is reacted with hydrogen and nitrogen atoms simultaneously.

33. The method of claim 30 wherein the metal precursor is tungsten hexafluoride and the film is tungsten nitride.

34. The method of claim 30 wherein the metal precursor is tantalum pentachloride and the film is tantalum nitride.

35. The method of claim 30 wherein the metal precursor is aluminum trichloride or trimethylaluminum and the film is aluminum nitride.

36. The method of claim 30 wherein the metal precursor is titanium tetrachloride and the film is titanium nitride.

37. The method of claim 30 wherein the metal precursor is silicon tetrachloride or dichlorosilane and the film is silicon nitride.

38. The method of claim 30 wherein the metal precursor is trimethylgallium and the film is gallium nitride.

39. The method of claim 30 wherein the first radical species are atomic hydrogen and steps (e) and (f) are united to one step using one or both of NH and NH_2 radicals, and the metal surface in step (f) is terminated with amine species reactive with the metal precursor to deposit the metal.

40. A process for building a metal, metal oxide, or metal nitride film on a substrate surface, wherein deposition steps comprising flowing a metal precursor gas or vapor over the surface with the surface terminated with a first chemical species reactive with the metal precursor to deposit the metal, are alternated with steps comprising flowing radical species over the freshly deposited metal layers to remove the ligands from the deposition steps and to provide the first chemical species to terminate the substrate surface preparatory to the next deposition reaction.

41. The process of claim 40 wherein a metal nitride film is built up by a step sequence of metal deposition by reacting a metal precursor gas with a surface terminated by amine species, then alternating exposure of the surface with atomic

radical hydrogen, nitrogen and hydrogen again, thereby volatilizing products remaining from the metal deposition chemistry, nitridizing the deposited metal monolayer, then terminating the metal surface with amine species again in preparation for a next metal deposition step.

42. The process of claim 40 wherein a metal oxide film is built up by a step sequence of metal deposition by reacting a metal precursor gas with a surface terminated by hydroxyl species, then alternating exposure of the surface with atomic radical hydrogen, oxygen and hydrogen again, thereby volatilizing products remaining from the metal deposition chemistry, oxidizing the metal monolayer, then terminating the metal surface with hydroxyl species again in preparation for a next metal deposition step.

43. A method for depositing a compound film on a substrate surface in a deposition chamber, comprising steps of:

(a) depositing a monolayer of metal on the substrate surface by flowing a metal molecular precursor gas or vapor bearing the metal over a surface of the substrate, the surface saturated by a first reactive species with which the precursor will react by depositing the metal and forming reaction product, leaving a metal surface covered with ligands from the metal precursor and therefore not further reactive with the precursor;

(b) terminating flow of the precursor gas or vapor;

(c) purging the precursor with inert gas;

(d) flowing a first radical species into the chamber and over the surface, the radical species highly reactive with the reaction product and combining with the reaction product to create volatile species and saturate the surface with the first radical species;

(e) flowing nonmetal radical species into the chamber to combine with the metal monolayer deposited in step (a), forming a compound film of the metal;

(f) flowing a third radical species into the chamber terminating the surface with the first reactive species in preparation for a next metal deposition step; and

(g) repeating the steps in order until a composite film of desired thickness results.

44. The method of claim 43 wherein the first and third radical species are both atomic hydrogen, and the metal surface in step (f) is terminated with hydride species of the nonmetallic element that are reactive with the metal precursor to deposit the metal.

45. The method of claim 43 wherein the non-metallic and hydrogen atomic steps (e) and (f) are repeated to improve the film quality.

46. The method of claim 43 wherein steps (e) and (f) are combined into one step wherein the surface is reacted with hydrogen and non-metallic atoms simultaneously

47. The method of claim 43 wherein the metal precursor is molybdenum hexafluoride or molybdenum pentachloride, the non metallic element is sulfur and the film is molybdenum disulfide.

48. The method of claim 43 wherein the metal precursor is zinc dichloride, the non metallic element is sulfur and the film is zinc sulfide.

49 A radical-assisted sequential CVD reactor, comprising:

a chamber with controlled gas inlets for introducing gases in sequential steps and a heated substrate support for holding a substrate and exposing a surface of the substrate to incoming gases; and

a plasma generation apparatus for generating radical atomic species for use in the reactor;

wherein an aggregate metal layer is formed by depositing a monolayer of metal on the substrate surface by flowing a precursor gas or vapor bearing the metal over a surface of the substrate. the surface terminated by a first reactive species with which the precursor will react by depositing the metal and forming reaction product, leaving a metal surface not further reactive with the precursor, terminating flow of the

precursor gas or vapor, flowing at least one atomic radical species into the chamber and over the surface, the atomic species highly reactive with the reaction product and combining with the reaction product, and also terminating the surface, providing the first reactive species, and repeating the steps in order until a composite film of desired thickness results.

50. The reactor of claim 49 wherein the atomic radical species is atomic hydrogen.

51. The reactor of claim 49 wherein the precursor gas bearing the metal is tungsten hexafluoride and the metal deposited is tungsten.

52. The reactor of claim 49 wherein the plasma generation apparatus comprises an electrode within the reactor chamber and a high frequency power supply connected to the electrode.

53. The reactor of claim 49 further comprising a showerhead-type gas distribution apparatus, and wherein a plasma is generated within the showerhead apparatus to produce the atomic radical species.

54. The reactor of claim 49 wherein the atomic radical species is produced in a remote plasma generator, and the species are delivered to the reactor.

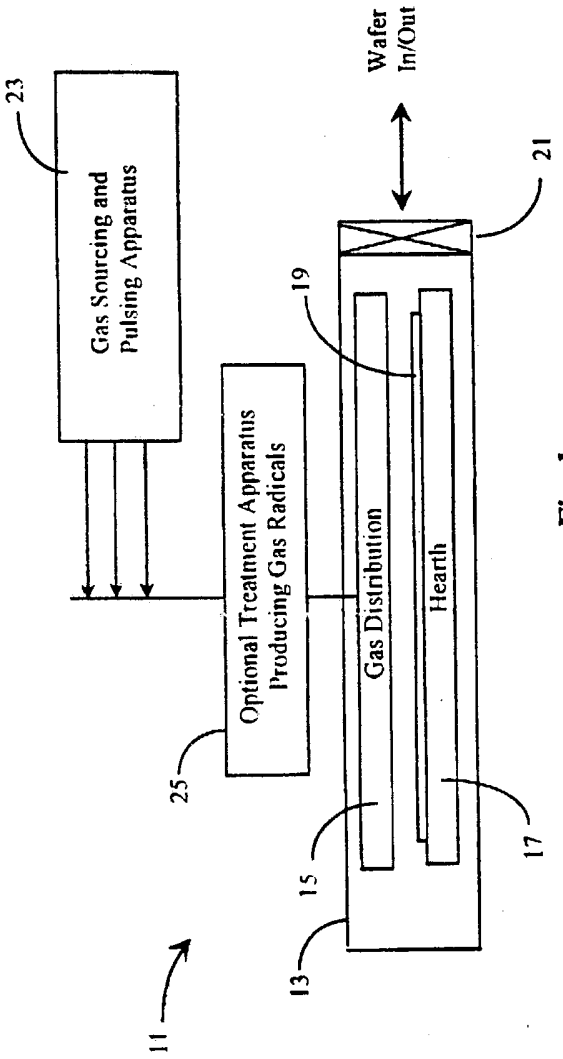

Wafer
In/Out
23
Gas Sourcing and
Pulsing Apparatus
21
19
Optional Treatment Apparatus
Producing Gas Radicals
Gas Distribution
Hearth
25
15
17
13
11

Fig. 1

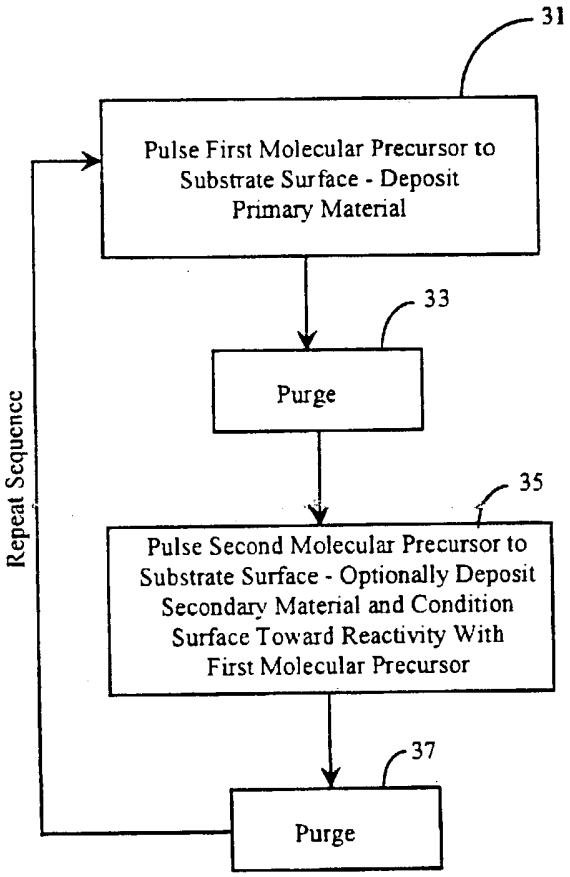


Fig. 2 - Prior Art

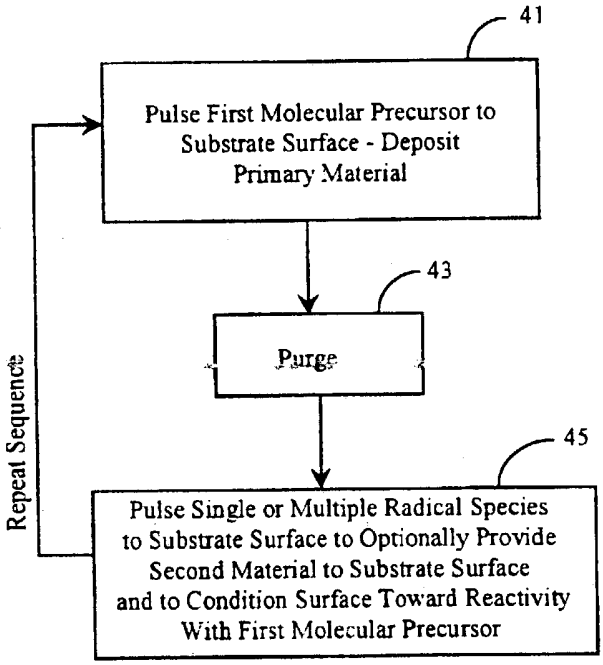

41
Pulse First Molecular Precursor to Substrate Surface - Deposit Primary Material
43
Purge
45
Pulse Single or Multiple Radical Species to Substrate Surface to Optionally Provide Second Material to Substrate Surface and to Condition Surface Toward Reactivity With First Molecular Precursor
Repeat Sequence

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/02577

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :H01L 21/44; C23C 16/00
US CL :438/685; 118/719
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 438/685, 680, 681, 679, 676; 118/719, 715, 723MP, 725

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

USPTO APS, DERWENT, JPO
search terms: molecular layer deposition, atomic layer deposition

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P — A,P	US 5,916,365 A (SHERMAN) 29 June 1999 (29-06-1999), col. 2, lines 10-18; col. 6, lines 5-43; col. 7, lines 45-68; and col. 8, lines 1-7.	1-11, 40-41, 49-50, 52, 54 — 12-39, 42-48, 51, 53
Y,P — A,P	US 6,015,590 A (SUNTOLA et al.) 18 January 2000 (18-01-2000), col. 4, lines 6-40 and 44-56; and col. 9, lines 13-45.	1-11, 40-41, 49-50, 52, 54 — 12-39, 42-48, 51, 53

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 MAY 2000	12 JUN 2000
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer CARIDAD EVERHART Telephone No. (703) 308-0956

Form PCT/ISA/210 (second sheet) (July 1998)*